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Solvent dependent Raman anisotropic bandwidth study in carbonyl containing molecule: Role of van der Waals' volume in intermolecular interactions

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Abstract · The bandwidths of the anisotropic Raman component (Γ_{aniso}) of Ethyl Acetate (EA) were measured for different solvent concentrations (ϕ) ranging from 10% to 90% using CH_3CN, $CHCl_3$ and C_6H_6 solvents and were plotted as a function of solvent concentrations. The data points are scattered and cannot be fitted into a particular curve. The data on anisotropic bandwidth are interpreted using the van der Waals' volume(V_w) within the framework of lineshape theory of Bratos and Tarjus The ratio (Γ_{aniso}/V_w) has been estimated and plotted as a function of ϕ This graph is an exponential curve in all the three solvents which shows that repulsive type of interaction forces $e^{-\alpha R}$ are responsible in the line broadening mechanism

Keywords . Vibrational relaxation, Raman bandshape, anisotropic bandwidth, van der Waals' volume

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1. Introduction

The intermolecular forces on molecular vibrations play a great role in the studies of dynamic processes and vibrational relaxation in molecular liquids[1-5]. The solvent-induced perturbations are reflected in the frequency and bandwidths of the vibrational bands of the solute molecule [1-4]. The van der Waals' volume has been taken into account to explain the intermolecular interactions based on the Bratus and Tarjus theory [6-9]. The C=O containing Ethyl Acetate(EA) molecule has been studied using CH_3CN, $CHCl_3$ and C_6H_6 solvents at different solvent concentration. Ethyl acetate is a compound having biological and chemical applications in industries and in research lab because of its unique characteristics.

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2. Experimental

Raman spectra were recorded for C=O stretching band of EA using CH_3CN, $CHCl_3$ and C_6H_6 solvents at various concentrations ranging from 10% to 90% using a Spex Ramalog 1403 double monochromator, a photon counting arrangement and a DM-3000 software. The 488 nm line from Spectra Physics model 165 Ar ion laser was used as excitation source. Laser power was maintained at about 300mW and slitwidth was kept at 2cm^{-1}.

The effect of finite slitwidth was corrected [10] by using the equation $\Gamma_t = \Gamma_a\left[1-(S/\Gamma_a)^2\right]$ where Γ_t and Γ_a are the true and apparent Raman linewidth (FWHM) respectively, and S is the spectral slitwidth in cm^{-1}.

3. Results and discussion

The bandwidths of the anisotropic Raman band (Γ_{aniso}) of EA were measured at different solvent concentrations ranging from 10% to 90% using polar and non-polar solvents (CH_3CN, $CHCl_3$ and C_6H_6) of varying dielectric constant. Figure 1 shows the spectrum of neat EA. The anisotropic bandwidths of EA in 3 solvents were measured at different solvent concentration. Figure 2 shows the variation of anisotropic bandwidth with solvent concentration. The data points are scattered and cannot be fitted into a particular curve. The data points show different patterns for each solvent at different solvent concentration however the data points are found to decrease at higher solvent concentration. The non-linearity of Γ_{aniso} showing in these plots from lower to higher solvent concentration may be due to the structural characteristics and the interacting nature of the substituents in the molecules. Investigations by D. Levesque, *et al* [11] as well as G. Tarjus and S. Bratos [6-9] show that for chemical solutions, the half width of isotropic and anisotropic

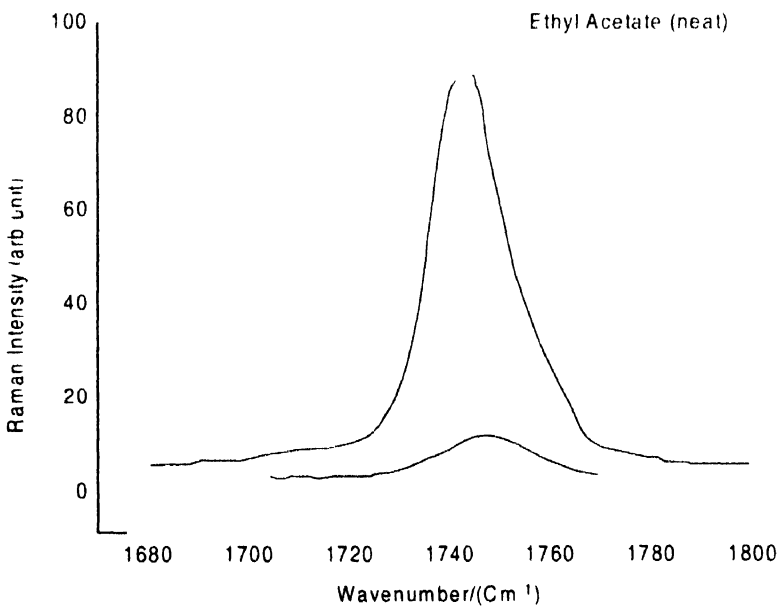

Figure 1. Raman spectrum of Neat Ethyl Acetate.

Raman bands is concentration dependent and this dependence is complex, even in the slow and fast modulation limits. This is due to the fluctuation of the chemical composition in a given site of the liquid and to the structure breaking effects[12-18].

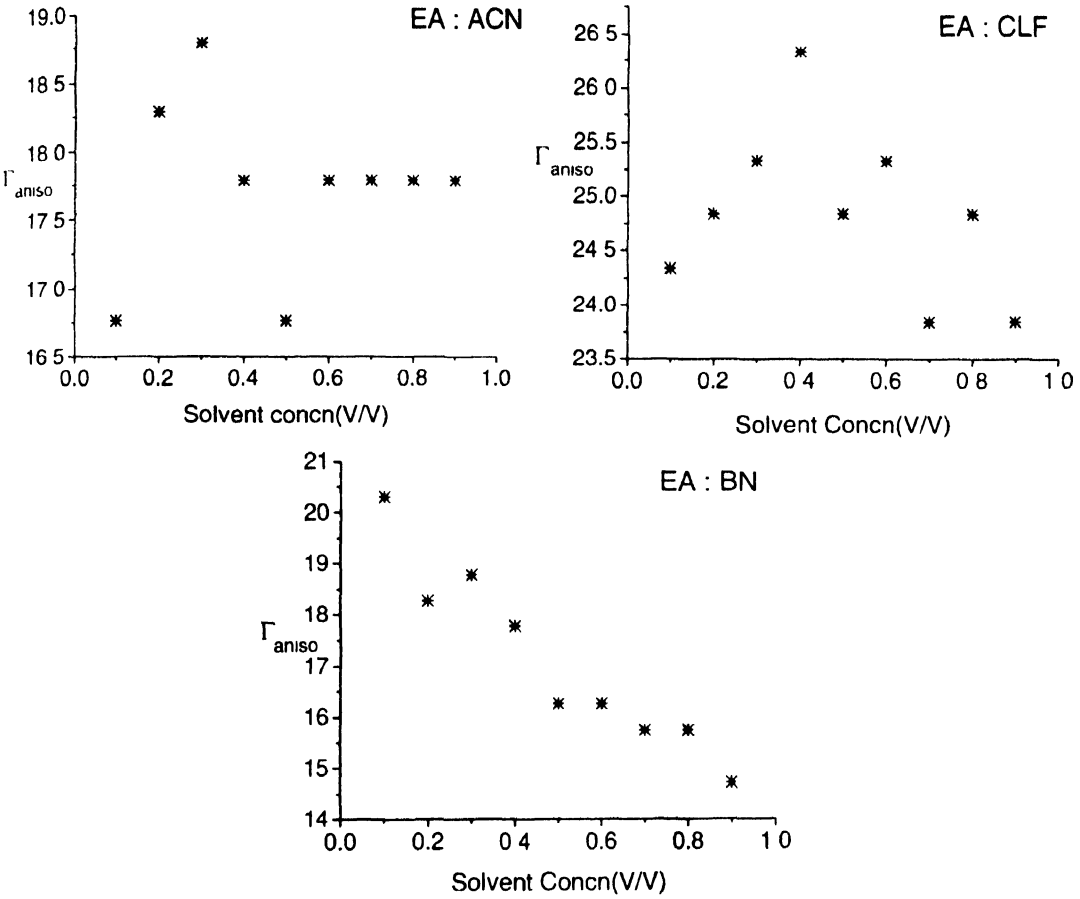

Figure 2. Variation of solvent concentration with the anisotropic bandwidth

The interaction energy due to solute-solvent interaction may arise due to the contribution from one or more coupling terms, such as dipole-dipole, dipole-quadrupole and quadrupole-quadrupole, dipole-induced dipole *etc.* [1,3-4]. In order to have a more clear picture about the intermolecular interactions involved we have taken into account the van der Waals' volume of the sphere of influence in a solute dissolved in different solvents. The calculation of van der Waals' volume assumes knowledge of bond distance; inter molecular van der Waals' radii [19] and shapes of atoms in various molecular configurations. The van der Waals' volume of the interacting system was calculated by using the equation

$$V_w = \Phi\, V_w(solute) + (1-\Phi)\, V_w(solvent)$$

keeping in view the varying nature of the solute-solvent distance in a liquid, where Φ is the concentration of the solute. The calculations for the van der Waals' volume of the

solute and solvent were done keeping in view of the fragments of the molecules, which may have closest approach. The main interaction is considered between the dipole, which is the C = O of the solute and the solvents which are of dipole, quadrupole and octupole in nature. For solute-CH_3CN system, the main interaction is likely between the dipole moment of C = O bond of the solute and the dipole moment of the solvent. When EA is dissolved in CH_3CN, the dipole-dipole interaction of the solute-solvent system will affect the pair interaction. The dipole of CH_3CN molecule will try to interact with the dipole of the solute and align along the electric field of the solute dipole. In this case, the closest approach is determined by the orientation of the C – C ≡ N fragment of the solvent molecule. However, the liquid nature of the system will maintain the smooth flow because the hydrodynamic forces may be dominant over the electrical forces. The cylindrical shape of the CH_3CN molecule may not hinder the smooth flow of the molecules; hence, the van der Waals' volume for the solvent has been taken for the entire molecule, which is the sum of van der Waals' volume of the C – C ≡ N fragment and the van der Waals' volume of CH_3 group[19]. For solute EA-benzene compound, the main interaction is between the quadrupole moment of solvent benzene and the C = O of the solute. Similarly, for the

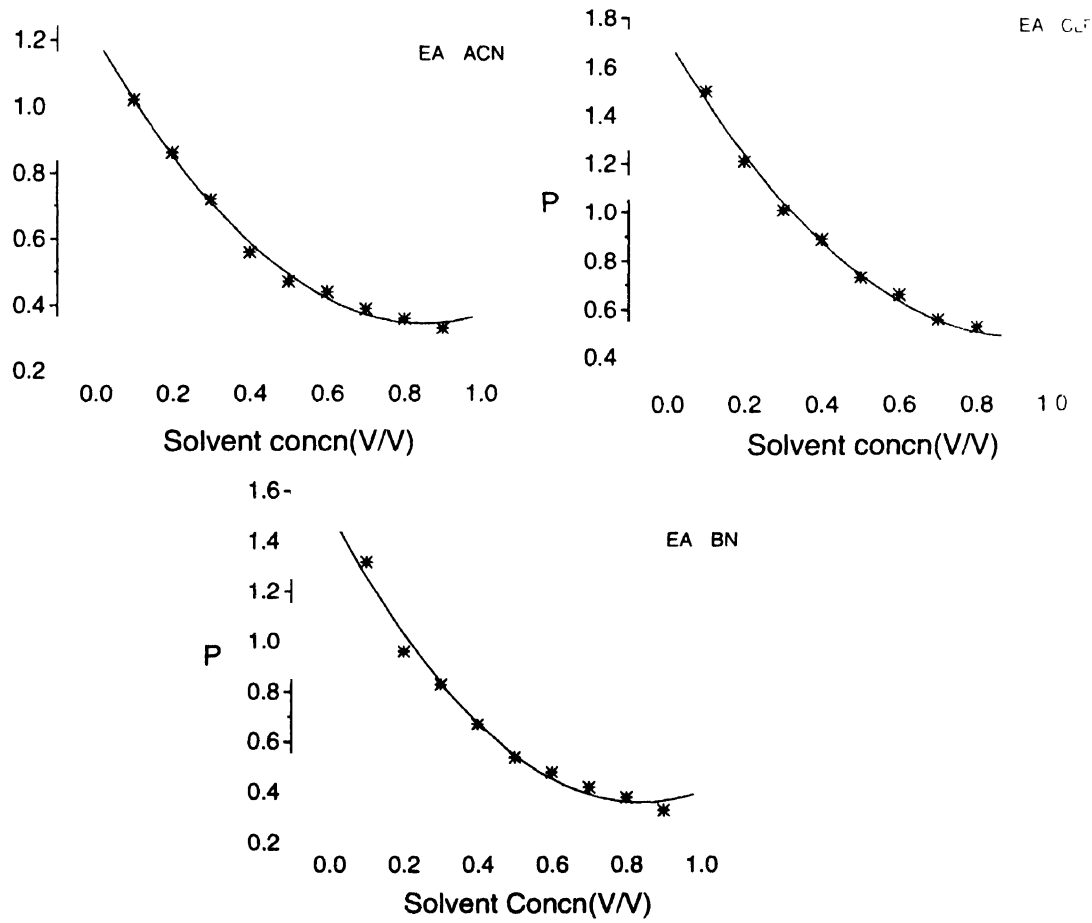

Figure 3. Variation of solvent concentration with the P.

interaction between EA – $CHCl_3$, the main interaction is taken between C = O and the entire solvent molecular structure as the hydrodynamic properties of the liquids have to be taken into account [1,3].Table 1 shows the calculated values of van der Waals' volume of solute and solvents using the data from Bondi [19]

Table 1 Van der Waals' volume of solute and solvent molecules

Molecules	C = 0 (Solute) cm^3/mol	CH_3CN (Solvent) cm^3/mole	$CHCl_3$ (Solvent) cm^3/mole	C_6H_6 (Solvent) cm^3/mole
Van der Waals' volume	11 7	59 44	55 93	48 4

The values of $P = (\Gamma_{aniso}/V_w)$ have been determined for each solvent and plotted as a function of solvent concentration (Figure 3) This graph is an exponential curve in all the solvents This indicates that the repulsive type potential $\exp(-\alpha R)$ may be playing a significant role

4. Conclusion

The Raman anisotropic bandwidths are interpreted using the van der Waals' volume (V_w) within the framework of lineshape theory of Bratos and Tarjus The van der Waals' volumes of molecular fragments of closest approach have been taken into account so as to explain the intermolecular interaction in liquids It has been found that repulsive type of intermolecular interaction is responsible for the solute-solvent systems

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